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Short Communication

Some physical properties of chitosan in propionic acid solutions

Esam. A. El-hefian, Rashid Atta Khan*, and Abdul Hamid Yahaya

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
*Corresponding author, e-mail: dr_rashid@um.edu.my

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Abstract: Surface tensions, contact angles and conductivities of propionic acid solutions containing different amounts of chitosan were measured at a room temperature to a temperature accuracy of $\pm 0.20^{o}$. The value of critical coagulation concentration (CCC) was then obtained from the plots of contact angle and conductivity versus concentration. Viscosity of the solutions with different concentrations was also measured in this work at the same temperature and from the plot of viscosity against concentration, the intrinsic viscosity was determined by extrapolation.

Keywords: propionic acid, chitosan, intrinsic viscosity, critical coagulation concentration

Introduction

Chitosan, $1 \rightarrow 4$ linked: 2 – amino-2-deoxy-β-D-glucan, is a modified carbohydrate polymer derived from chitin by deacetylation [1]. It is also known as soluble chitin. Due to the amino groups that chitosan possesses in its chain, it can be dissolved in dilute aqueous acid solutions such as acetic acid and propionic acid. Chitosan is described in terms of the average molecular weight and degree of deacetylation [2, 3]. Chitosan has been extensively used over a wide range of applications. As a matter of fact, many of chitosan's applications depend upon its unique properties such as biodegradability and non-toxicity. For instance, it can be used in wastewater treatment, medicine, food and cosmetics [4-9]. A lot of work has been done on chitosan. However, the literature is still relatively poor with respect to the physical properties of this polymer [10].

The objective of this work is to study some physical properties of chitosan in propionic acid solutions with a view to further explore the thin film properties and its applications.

Materials and Methods

Materials

Shrimp-source chitosan (95-97% deacetylation) was used in this work. It was provided by the chitin-chitosan laboratory of Universiti Kebangsaan Malaysia (UKM). Propionic acid used in this work was of 98% purity. Distilled water was used to prepare all solutions.

Methods

The k122 processor tensiometer was used for the determination of surface tension. The surface tension was determined by the plate method. Calibration of the instrument was done with distilled water. The platinum wire was cleaned before every measurement by ethanol, then rinsed with distilled water and finally dried by momentarily heating in a luminous flame. Contact angle of the samples was measured using the contact angle measuring system G40 at 28^{o}C. The measurement was done on microscope slides (25.4 × 76.2 mm, 1-1.2 mm thick). Each slide was cleaned before use by soaking in ethanol overnight. The average contact angle of both sides of the drop was taken into consideration, the average value of which was 42^{o}. Volume of sample used was 1 μL and the measurement time was 1.5 minutes.

Conductivity measurements were carried out using the Orion Model 105 Conductivity meter. The actual conductivity reading is obtained by multiplying the observed conductance (observed reading) by the cell constant (K), which is equal to 1.0 cm^{-1} in this case. Calibration was done with standard potassium chloride solution.

Ubbelohde type viscometer was used to measure the viscosity. Flow time was recorded automatically using a viscoclock (Schott ViscoClock). Each value was an average of about 4 measurements. The average values of the intrinsic viscosity was taken by extrapolating the graphs of the inherent viscosity, $\frac{\ln \eta_r}{C}$, and the reduced viscosity, $\frac{\eta_{sp}}{C}$, versus concentration to C=0.

In order to achieve maximum possible accuracy, all the values taken were repeated five times and then an average was taken.

Results and Discussion

Surface tension of chitosan in 0.02M propionic acid solutions

The values of surface tension at various concentrations of chitosan in 0.02M propionic acid do not show any significant change over a wide range (Figure 1). This suggests that chitosan is fully dissolved in 0.02M propionic acid solutions and that there are no chitosan molecules at air-solution interface (no interfacial activity). This behaviour of chitosan in propionic acid is different from that in acetic acid and formic acid [11].

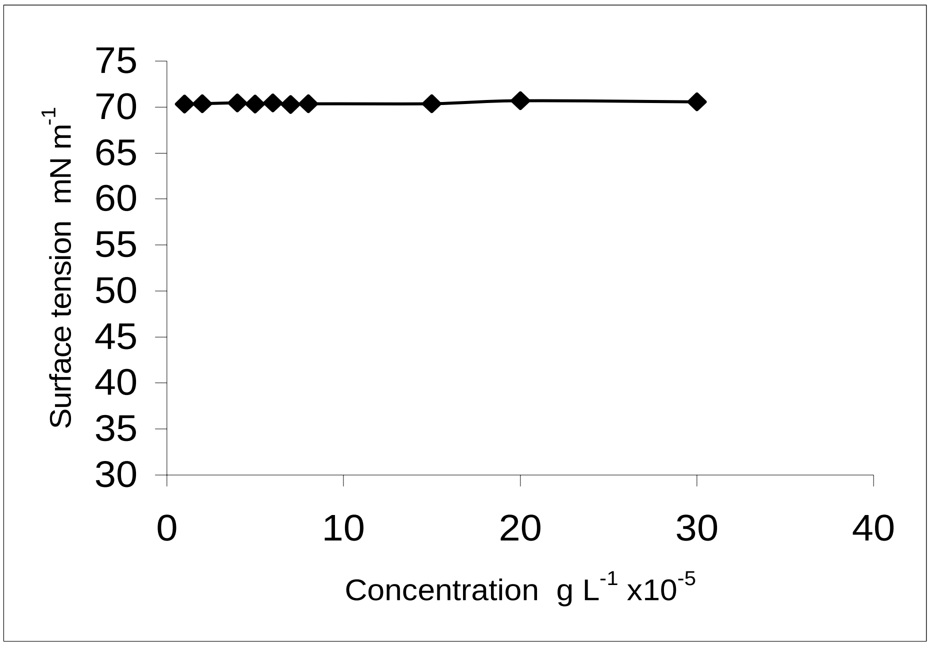

Figure 1. Plot of surface tension of chitosan in 0.02M propionic acid.

Contact angle of chitosan in 0.02M propionic acid solutions

The average contact angle is plotted as a function of concentration. As the concentration increases, the contact angle increases ($\cos\theta$ decreases) (Figures 2) until a critical coagulation concentration (CCC) is achieved and the contact angle becomes independent of concentration. The value of CCC is about 4.5×10^{-5} g L^{-1}.This phenomenon of chitosan solution in propionic acid is similar to that in formic and acetic acid solutions [12].

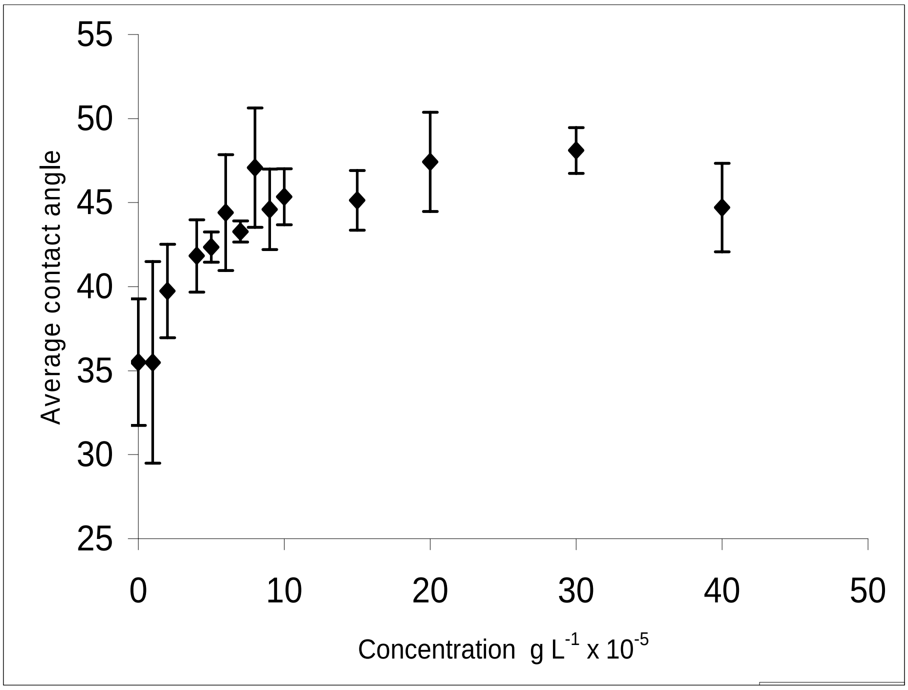

Figure 2. Average contact angle of chitosan in 0.02M propionic acid versus concentration.

Conductivity of chitosan in 0.02M propionic acid solutions

Figure 3 shows the correlation between equivalent conductivity and concentration. Equivalent conductivity decreases rapidly with increasing concentration until a critical coagulation concentration is obtained, from where it starts decreasing gradually (almost constant), which indicates that aggregation has occurred, but it is not that significant. From this profile, the CCC value estimated was 5×10^{-5} g L^{-1}. Interestingly, this value closely corresponds to that estimated from the contact angle measurement.

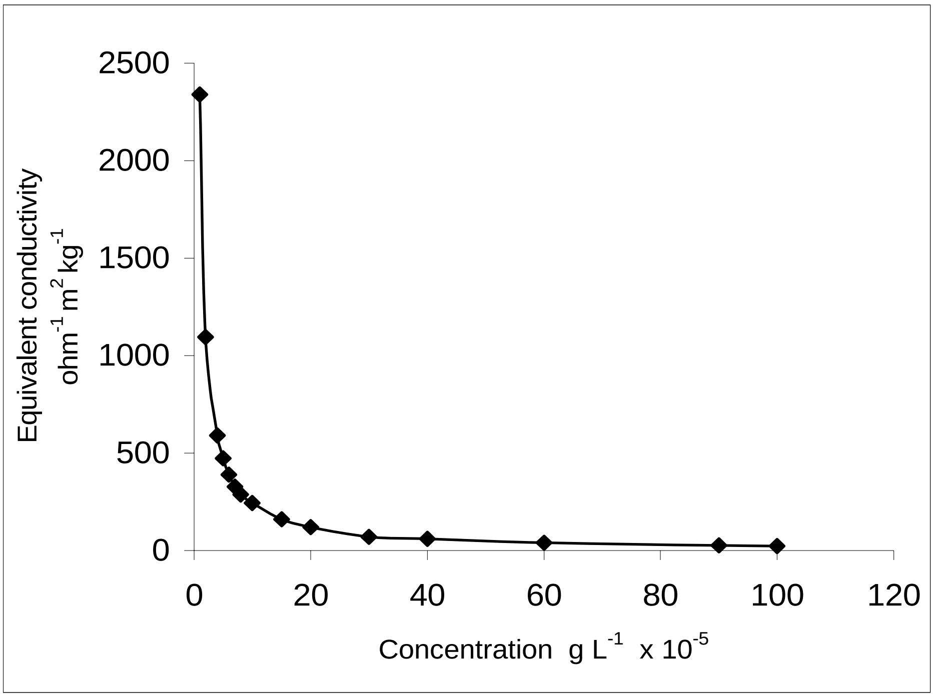

Figure 3. Equivalent conductivity of chitosan in 0.02M propionic acid versus concentration.

Viscosity measurement

The value of intrinsic viscosity, η, can be obtained by extrapolating the linear portion of the graph to $C = 0$ (Figure 4). This gives the value of intrinsic viscosity of 3.7679 x 10^3 cm^3 g^{-1}, which is higher than that found in other acids. Also, contrary to the normal behaviour, the viscosity of chitosan in propionic acid solutions decreases with concentration. Presumably, the interactions among the charge carriers could be the possible answer for this abnormal behaviour.

The values of coefficients k_1 and k_1', which were calculated from the slopes, are 7.85 x 10^{-2} and 4.87 x 10^{-2} respectively. It is accepted that the difference (k_1- k_1') can be higher or lower than 0.5 [13, 14].

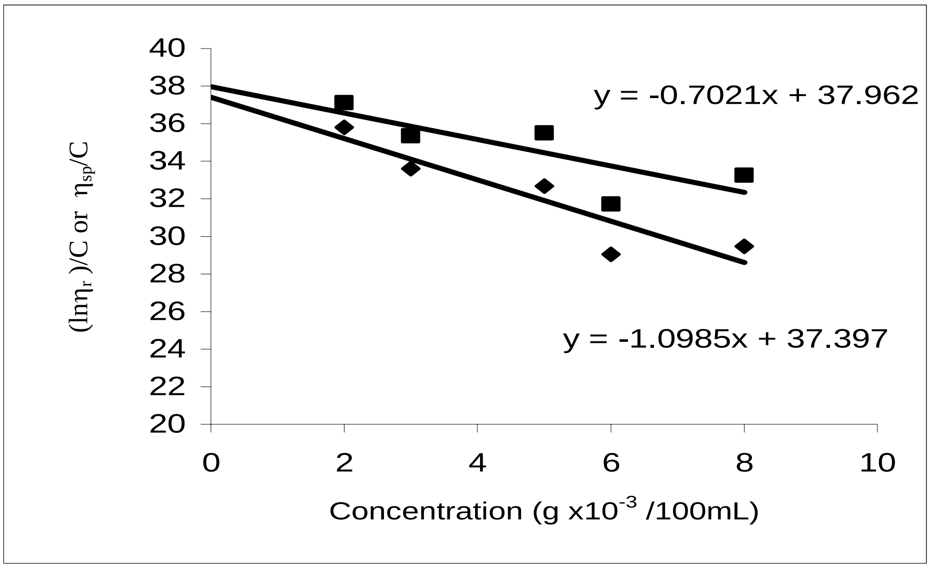

Figure 4. Inherent viscosities ($\frac{\ln \eta_r}{C}$) and reduced viscosities ($\frac{\eta_{sp}}{C}$) of chitosan in propionic acid solutions versus concentration.

Conclusions

The following conclusions can be drawn from this study.

1. Unlike chitosan in formic and acetic acids, that in propionic acid solutions is fully dissolved and shows no surface activity. However, they all show similar behaviour with respect to contact angle and conductivity measurements.
2. The intrinsic viscosity of chitosan in propionic acid is quite high. In addition, the viscosity of chitosan in propionic acid solutions decreases as a function of concentration.
3. In the design of suitable experimental conditions, the predetermined physical properties and behaviour of the chitosan in above mentioned acids could play a significant role.

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